I. The Action of Hydrochloric Acid Gas upon Metallic Vanadates.

II. The Occurence of Molybdenum in the Mineral Endlichite.

THESIS

Presented to the Faculty of the University of Pennsylvania
In Partial Fulfillment of the Requirements
for the
Degree of Doctor of Philosophy

BY

GILBERT HILLHOUSE BOGGS, B. Sc.
UNIV. OF GEORGIA

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I take great pleasure in expressing my deep appreciation of the ready council and lasting inspiration received from my friend and teacher, Professor Edgar F. Smith.

SECTION I.

The Action of Hydrochloric Acid Gas on Metallic Vanadates.

INTRODUCTORY.

The halogen hydrides, in gaseous form, are capable of wide application as analytical reagents, and considerable work has been done already in this laboratory with a view to the extension of their uses. Of the four acids, hydrochloric, because of its stability and ease of generation, is the most used.

One of the initial experiments leading in this direction was reported by Debray (Compt. Rend., **46,** 1098. Annalen **108,** 250), and it describes the complete volatilization of molybdenum trioxide when heated in a stream of hydrochloric acid gas.

Later E. Pechard (Compt. Rend., **114,** 173; Zeit. anorg. Ch. **1,** 262) used this property as a basis of a method for the separation of molybdenum; and Smith and Oberholtzer (J. Am. Ch. Soc. **15,** 18) verified and extended his work. The atomic weight of molybdenum was also determined by this action of hydrochloric acid gas, by Smith and Maas (Zeit. anorg. Ch. **5,** 280).

Turning to vanadium, Smith and Hibbs (J. Am. Ch. S. **16,** 578; Zeit. anorg. Ch. **7,** 41) found that sodium vanadate behaved similarly to sodium molybdate; and the other

members of Group V. of the periodic system were the object of a study by the same authors (J. Am. Ch. S. **17,** 682), while Smith and Meyer (J. Am. Ch. S. **17,** 735) reported investigations as to the actions of the other haloid acids.

Of the elements so studied, nitrogen, vanadium, arsenic, antimony, and columbium were found capable of complete volatilization from their salts, but phosphorus and tantalum were not at all so affected. Jannasch and Schmitt (Zeit. anorg. Ch. **9,** 274) have confirmed some of this work.

Up to that time the oxygen derivatives of these elements were the only compounds investigated, but a discovery by Keeley and Smith (J. Am. Ch. S. **18,** 1096) of the volatility of arsenic sulphide in this acid gas led to the successful separation of it from the non-volatile vanadium sulphide by Smith and Field (J. Am. Ch. S. **18,** 1051).

In 1896, Moyer (Thesis, Univ. of Pa.) announced the following successful separations by the same method: bismuth from lead and copper; antimony from lead and copper; arsenic from lead, copper, cadmium, silver, cobalt and nickel.

Hydrobromic acid gas, in the hands of E. A. Atkinson (Thesis, Univ. of Pa., 1898), gave quite as uniform results, there being some modifications of time requirements and of composition in the volatilized products.

The sulphides of antimony and tin were the subject of a study by Keeley and Smith (J. Am. Ch. S. **18,** 1096). Other sulphides by Moyer (J. Am. Ch. S. **21,** 642), and Tunnell and Smith publish in the same volume, page 929, an article on the action of hydrochloric acid gas on the sulphates, selenates, tellurates and phosphates.

Having in mind these quite fruitful investigations already reported from this laboratory, the experiments recorded

in the pages to follow were instituted with the hope that a broadly applicable method would be found, whereby the element vanadium could be isolated quantitatively from various synthesized compounds, and the method then be extended to the very complex minerals in which the element may occur.

Those who have handled vanadium in an analytical way would readily appreciate the usefulness of a clean and rapid method for its separation, and such a discovery would prove most useful. The modern text-books on analytical chemistry, and compilations of even greater pretensions, as a rule either fail to give any methods of separation, or hopelessly confuse one by the inapplicability and obsoleteness of those given.

The apparent justification of this deficiency may be found in the plea that vanadium is comparatively rare as an element, and hence infrequently met with in mineral analyses.

The real cause is more likely the great lack of careful and exhaustive study of the reactions of vanadium, with a view to its separation; and those who are working in the mineral field with the object of ascertaining not only *what* is present, but just *how much* of the constituent is there, must face this problem with regard to vanadium, if they have not already done so. The coming question of the constitution of minerals needs for its solution the valuation of these rarer elements.

The chemists of the United States Geological Survey, under the wise direction of Messrs. Clarke and Hillebrand, have done much by experiment, and in print, towards showing the inadequacy of the old routine methods of rock and mineral analyses. The latter often fail to report certain persistently occurring elements because of their small quantities, and have thus escaped the notice of the analyst. To quote Prof. Clarke's words, from the Introduction to Bul-

letin No. 148, of the Geological Survey; speaking of the old "complete analysis" scheme, he says: "* * * only the main constituents, those having direct petrographic significance, were determined. In such analyses, the minor ingredients, like titanium, phosphorus, barium, strontium, chlorine, etc., were ignored; and although the results are satisfactory in some respects, they leave much to be desired. Latterly, greater completeness has been sought for, the work done has been much fuller, and the data obtained can be discussed with much higher approaches to accuracy. The old form of 'complete analysis' is to be discouraged; it leads too often to erroneous conclusions, and only the best modern methods of work and statement should be tolerated. The fuller analyses, moreover, have brought some interesting points to light; titanium now appears to be one of the more abundant elements, and barium and strontium are found to be almost universally diffused in igneous rocks, in quite perceptible quantities."

Prof. Clarke gives numbers of illustrations of the differences made by the older, and less careful, methods as to the contents of various rocks.

To the list placed in this Bulletin (1897) may be added, among others, molybdenum and vanadium, as being more widely distributed in nature than formerly thought, though in small quantities, often. And it is quite conceivable that traces are often obscured to the ordinary analyst by the overwhelmingly larger quantities of other elements, some of which may be closely enough related to them to prevent, by mass action, characteristic reactions.

Such difficulties as indicated place severe conditions and limitations upon methods laying claim to great efficiency as means of detection and isolation of these elements. However, such was the ambition of this investigation, at least as regards the element vanadium.

Many of the analytical methods proposed for the separation and estimation of vanadium have been compiled by Hintz and Weber (Zeit. für anal. Ch. **32,** 217; Chem News, **70,** 157, 168, 178, 190). And, since molybdenum becomes of some importance in this paper, it may be well to add that it is treated similarly by Brearly (Chem. News, **78,** 203; **79,** 2, 14), and by Friedheim and Euler (Ber. **28,** 2061; Zeit. für anal. Ch. **35,** 77). See also Gooch and Norton (Am. J. Sc. **6,** [1898]; Chem. News **78,** 207).

It may be said of these methods that, not being within my personal experience, they are beyond my criticism. However, they appear hardly applicable to the requirements of ultimate, complete mineral analysis.

Before turning to the experimental part of this work, it may not be out of place to make a few observations and deductions on the methods and results hereafter described.

As may be surmised from the preceding historical sketch, the nucleus of the investigation undertaken was dependent on that property of vanadic acid which allows its expulsion from sodium vanadate by a stream of hydrochloric acid gas (Smith and Hibbs, loc. cit.). To this beginning must be added the encouragement received when Pullman (Thesis, Univ. Pa., 1898, not yet in print) found that apparently the mineral endlichite yields its vanadic acid readily to such treatment, requiring only that the vanadium must be separated subsequently from arsenic (Smith and Field, loc. cit.). A clean separation in such a case was a favorable indication as to results in applying the method; especially, since the mineral named is of a complex nature, being a chloro-arseno-vanadate of lead, with some other bases, and phosphorus in traces.

That the end attempted was not attained, is proclaimed discouragingly enough by the quite uniformly negative results to be reported. But as some unusual phenomena come up for explanation, and several "long felt wants" re-

assert themselves, perhaps enough of value may be attached to their discussion to be a sufficient apology for an otherwise barren research.

The first lesson one may learn from the following pages is an old one, and that is: the desirability of ascertaining first the precise composition, qualitatively of a substance (a mineral more especially) before reporting a "complete" quantitative analysis of the same. This may necessitate the trouble of a qualitative preliminary, which Prof. Clarke thinks "a sheer waste of time" in the case of rocks, but there is no doubt that in the case of endlichite, a thorough testing might have revealed molybdenum at first, and saved a great deal of time and patience. It is true that manganese and aluminium were discovered in the course of a regular quantitative scheme, though not reported in previous analyses I had seen, but this elusive element, molybdenum, was brought to the light only after special and direct testing. So far as is known, it has never been reported previously in that mineral.

The importance of this point may be seen easily when it is said that molybdenum had at no time been suspected, although the same sample had been through the hands of more or less experienced analysts for several years, and some results added up to the too usual 100 per cent. without it, though much of that reported as "vanadic acid" is probably molybdic acid.

Moreover, when a substance is the source of material for atomic weight work, the point is greatly emphasized. From this endlichite was obtained all the vanadium to be had for investigations. Such material was used to prepare a large quantity of vanadic acid to be used in atomic weight investigations of vanadium, without, of course, using special precautions for the elimination of molybdenum, which would otherwise contaminate the former, and partly ac-

count for the high results obtained. And yet a clean separation of the two is a problem not yet beyond the qualitative stage perhaps.

This leads up to a point of great importance: as to the tests for distinguishing the elements, separately and together. The confusion is increased since it is established that it is possible enough that they occur associated.

When the substance to be tested is in solid form, the test given in the last American edition of Fresenius' Qualitative Analysis is a good one, though no record is given as to its delicacy. The powder is treated with a few drops of concentrated sulphuric acid and heated to fuming. When cool, add a few drops of alcohol, and the appearance of a deep blue coloration indicates the presence of molybdenum, distinguishing it from vanadium, tungsten or titanium. The limitation to solids, however, lessens the general value greatly.

In Dammer's "Handbuch der anorganischen Chemie," among the tests given for molybdenum is one requiring the addition of a solution of potassium xanthate to the solution to be tested, after previously acidifying with sulphuric acid. If fair amounts of the element be present, there is a pink precipitate which soon changes in color to a dark blue, while in dilutions as high as 1:500,000 a very perceptible pink coloration appears. I have tested this method with molybdates, and find it extremely delicate, and so far as experiments have gone, is operative in the presence of small quantities of vanadium. But the strong yellow color of free vanadic acid in larger amounts obscures the test for molybdenum.

Throughout the greater part of this research, Werther's hydrogen peroxide test was used for vanadium, it being of easy and rapid application, and far more delicate than the bead or reduction tests. It consists in merely acidifying the solution analyzed, preferably with dilute sulphuric acid,

and adding a few drops of a solution of hydrogen peroxide. A red coloration indicates vanadic acid.

However, there are important limitations on this test. (1) It is not very useful in solutions having color already, such as from nickel, cobalt, manganese, or strong ferric iron. (2) Simultaneous color reactions with chromium, molybdenum or titanium derivatives which may be present in the same solution. As to the first point, it may be said that the effect of slight tints from manganic or ferric salts may be overcome by comparing the solution tested against itself, and one can soon learn to distinguish the reaction. But in the presence of strong colors from nickel and cobalt, it is best to eliminate these metals first. The interference of chromium and titanium is not so likely to be met with, but, as proven in this investigation, molybdenum may be present, and on account of its brown or yellow color reaction with hydrogen peroxide may be confused with the vanadium test, even being mistaken for traces of the latter. The ether solubilities of such colors may prove helpful in establishing a distinction, but as molybdenum was not suspected in this work until the end, the distinction was not sought for.

How far the results given in this paper have been distorted by the presence of molybdenum in the solutions tested, is as yet not known, since most of the compounds synthesized were consumed entirely before the possibility of such a factor was realized. However, it is known that molybdenum was present in some of these salts, and that probably the others contained it also, though to a less degree.

As far as is known, no study has been made as to the nature of the volatile vanadium compound obtained when vanadates are exposed to the action of hydrochloric acid gas. The solution of this, doubtless, difficult problem is made more urgent by the unsatisfactory separations obtained.

The fact that one gets a sublimate in the case of molybdenum which can be isolated and analyzed, accounts for the ready report of its composition. But vanadic acid yields gases, or liquid bodies so volatile that they are destroyed or modified by the water vapor given off at the same time. And then, a partial reduction seems to take place in the vanadates, chlorine is evolved, and part of the vanadium remains behind as a lower oxide. It is worthy of note in this connection that Gibbs, some years ago, observed a similar behavior of concentrated hydrochloric acid solutions of vanadates, in that chlorine was evolved on heating and a green solution of a lower oxide remained. Gibbs proposed this as a method for determining vanadium.

Finally, it is most interesting that of the compounds so far studied, two only seem to give up all their vanadic acid to hydrochloric acid gas. One of these is a simple sodium pyro-vandate (Smith and Hibbs, loc. cit.), and the other the complex mineral, endlichite, studied by Pullman (loc. cit.). Though these lie at opposite poles as to structure, the intermediates seem to act entirely differently. Pullman's separation has been verified by me in the prosecution of this work.

The greatest interest is focussed on the lead compounds. The simple salts of this metal do not seem to behave like the compounds found in endlichite, but fall into line with the others giving negative results. But closer study reveals the presence of molybdenum in this endlichite; while a vanadinite, reported as having the same qualitative composition, but which was found free from molybdenum, would not yield up all its vanadium as did the endlichite Some always remained behind as a lower oxide.

The question now arises as to what relation there can be between the removal of vanadium from endlichite (molybdenum being present), on the one hand, and the failure to do so from vanadinite (in the absence of molyb-

denum), on the other. And, again, why should it leave sodium vanadate so readily, and not leave barium or aluminium, for instance?

Are these acids present in endlichite as a molybdenum-vanadium-arsenic complex which can be removed as a whole from the mineral, or, does the molybdenum or the arsenic merely drag out the vanadium in its own hasty exit? Can the presence of one or both of these others prevent the reduction of vanadic acid to the lower oxide, which is involatile? If so, why can it be removed from sodium vanadate without such means?

Having thus considered the historical and more or less speculative sides, it now remains to present the experimental basis upon which the other should rest for verification.

EXPERIMENTAL.

Under this sub-title will be considered:

1. Sources of, methods and apparatus for preparing the vanadic acid.

2. Detailed record of the various experiments attempting the separation of vanadic acid from iron, aluminium, manganese, zinc, barium, lead, nickel and cobalt.

1. *Sources, Etc.* As previously indicated, the vanadic acid used for this work was derived primarily from the mineral endlichte, said to be a vanadate and arsenate (1:1) of lead, containing chlorine, and various bases in small amounts. A large quantity of the mineral had been bought through a local dealer some years since, and no record of its source is now accessible.

The material as placed in my hands consisted of a dark green liquid, chiefly hydrochloric acid, mixed with a pasty mass which seemed to be gangue and residues from previous operations on endlichite, the green color being due to lower oxides of vanadium.

In order to oxidize thoroughly and set free as much vanadic acid as possible, the whole was repeatedly evaporated to dryness with nitric acid, until a uniformly brown mass was obtained. This was heated carefully until dry and then pulverized. In order to separate the vanadic acid from this mass, it was determined to heat it a portion at a time, in a stream of dry hydrochloric acid gas, and catch the volatile matter in water, from which the vanadium could be recovered by evaporation.

The aparatus necessary for such operations has been described frequently in articles quoted herein, and no details will be given. Briefly it was this: (1) A generator for hydrochloric acid gas of such capacity as to run hours without renewal; (2) a drying system for the gas; (3) a Bunsen burner, the four tubes of which were set in a row, as in a combustion furnace. Each tube had its own gas cock, and the base of the burner supported a framework bearing a short iron trough, lying above the flames at an adjustable distance. The volatilization was carried on in a hard glass tube lying in the trough. The anterior end of the tube was drawn out to a size suitable to enter a rubber stopper, and was then bent to a right angle, and fitted to a five-inch U tube, the latter acting as a suitable receiver, without danger of allowing the contents to be drawn into the combustion tube. For safety, two more U tubes were connected in series with this one, and all were partly filled with water.

Porcelain boats of medium size served to hold the substance acted on, and after introducing these, the generator system was connected up, the gas started and a gentle heat applied. The latter was sufficient to prevent any condensation in the tube. The burner just under the boat was gradually raised to its capacity.

The treatment of the material in this way proved a long and tedious operation, owing to the limited quantities used for each instalment. If amounts so great as a boatful were used at one operation, much vanadium remained behind as a lower oxide, which high heat and long treatment failed to remove.

When all the receiver liquids were combined and evaporated to dryness, there remained a greenish mass which required repeated evaporations with nitric acid before it assumed the red-brown color of vanadic acid. This crude product was dissolved in ammonia water, and precipitated

as ammonium metavanadate by a large excess of ammonium chloride. The precipitate was dried and ignited gently to expel the ammonia, leaving the vanadic acid as an orange red fusible mass. Some reduction accompanied this operation also, making necessary a repetition of the nitric acid treatment. It would seem that most vanadic acid, especially in presence of hydrochloric acid, is quite sensitive to reducing agents, or dust.

By these operations there finally resulted about thirty grams of what was assumed to be pure vanadic acid. This was dissolved in water acidulated with nitric acid and then diluted to a definite volume so that an approximate value was obtained of the strength of the solution.

All precipitated vanadates hereafter mentioned were made with this solution. Those described as made by fusion contained vanadic acid of a less pure sort, added to the fusion in solid form. This latter contained therefore more molybdenum.

Individual preparations and methods will be described as they come.

2. *Detailed record of various experiments attempting separations.*

Combinations of vanadic acid with the following metals were subjected to several experiments each, with modifications and repetitions wherever they seemed advisable.

No special apparatus was used in conducting these analyses, other than has been already fully described, no new conditions demanding alterations for qualitative work.

To insure truthful reports, tests for separations were made in good light, and repeated wherever doubtful.

The earlier experiments on iron and aluminium were carried on together, and before the hydrogen peroxide test had been adopted, and hence the reports are not so reliable perhaps. The slowness or awkwardness of other tests caused its exclusive use thereafter.

Vanadic Acid from Iron.

When iron is precipitated as hydrate in the presence of certain acids or their salts, it will take up more or less of them, depending on their nature and the conditions of mass action. This property was used as a basis for preparing compounds of iron and vanadic acid. Experiments showed that several times the equivalent amount of iron must be used in order to bring down all of the vanadic acid.

The precipitate, which did not differ from the ordinary ferric hydrate in appearance, was washed, dried, ignited and pulverized. Amounts of from 0.1 to 0.3 gram were used in the following experiments.

Exp. 1. About 0.1 gram was placed in the apparatus as described, and the current of gas started at a fair rate of speed. The reaction began so soon as the acid vapors reached the boat, and vanadium was carried off rapidly and collected, to some extent, with the condensed reaction water. With the application of gentle heat, there was a marked intensification of the reaction, and chlorine was evolved, indicating a reduction. [Jannash and Schmitt have noticed the reduction of ferric oxide to ferrous chloride in hydrochloric acid gas. See also Moyer (Thesis, p. 16).]

When no more volatilization was apparent, the apparatus was allowed to cool and then the receiver contents tested for iron, which was found, but that for vanadium by means of zinc and sulphuric acid was not conclusive.

Exp. 2. The acid gas acted in the cold first for about one hour, when no more vanadium seemed volatilizing. There was quite a crust of ferric chloride in the boat, but no iron could be detected in the receiver. So soon as reaction water began to collect in the boat, gentle heat was applied, at which the contents liquified partially. At the

end of the second hour, ferric salts had crept out of the boat, but the heat was not sufficient to carry any iron into the U tubes. The apparatus was then allowed to cool, and the acid gas discontinued. The liquid mass in the boat began to crystallize in beautiful iridescent green plates, which disintegrated on standing over night in a desiccator, leaving a brown crust. A second treatment in hydrochloric acid gas, at a gentle heat, caused a repetition of the melting and crystallizing phenomena, and during this action more vanadium was expelled. After forty-five minutes the experiment was discontinued, and the tests made. The receiver showed the presence of iron, but no vanadium by the zinc reduction test. Then a portion was digested with ammonium sulphide and treated with an excess of acid, which gave the brown vanadium sulphide. Meanwhile, the boat contents had again reverted to the amorphous form with a simultaneous evolution of hydrochloric acid.

Since iron was in the receiver, the separation was incomplete.

Exp. 3. The procedure was almost the same as in Exp. 2. At the end, vanadium was found in the residue, and iron in the receiver.

Exp. 4. No heat was applied for the first half hour, after which it was, with increasing intensity, for an hour. While no iron was found in the receiver at the end of this time, the tests for vanadium in the residue could not be made definite.

Exp. 5. Another portion of the material was subjected to an hour's action of the gas in the cold. A portion of the residue was then treated with water, the solution filtered off from insoluble matter, and after precipitating the iron with ammonia, the filtrate from this was tested for vanadium with *hydrogen peroxide.* None was found though the test was not reliable, since the iron precipitated

might have carried it down. The water extract of the residue in the boat was tested with hydrogen peroxide by comparing on itself, and although somewhat tinted by ferric chloride, a distinct reddening was observed, indicating vanadic acid. A test on ferric chloride alone failed to give a corresponding change.

This experiment seems to indicate that long action in the cold alone will not accomplish a separation.

Exp. 6. The conditions of the last attempt were modified in this case, in that the treatment in the cold was followed by half an hour's very gentle heating. At no time did the heat rise sufficiently to make the tube unbearably hot.

This experiment lasted for a total period of about one hour and a half, and finally the hydrogen peroxide test showed vanadium in the residue. Therefore a separation was not accomplished.

Exp. 7. Those who have worked with this method on vanadium heretofore have found its removal greatly expedited by a previous evaporation to dryness with nitric acid. Therefore, after subjecting the material to the action of hydrochloric acid gas for half an hour, using gentle heat, the boat was removed and a few drops of concentrated nitric acid added, but the reaction was so violent as to cause loss by spurting. The mass was dried thoroughly and then replaced in the gas apparatus as before, again using mild heat, and though considerable vanadium was volatilized some remained in the residue and gave the test with the peroxide. The separation was further negated by the presence of iron in the receiver.

Exp. 8. In previous experiments the soluble part only of the residue in the boat was tested. In this case, after the acid gas had acted for an hour, using moderate heat, the soluble portion of the boat's contents was apparently free from vanadium, but it was found in the insoluble por-

tion. The solution of the latter was effected by digesting several days with aqua regia.

Exp. 9. Not completed.

Exp. 10. The foregoing trials seem to indicate the interference by protecting layers of ferric or ferrous salts formed during the reaction. Therefore in this experiment, after the gas had been allowd to act for forty minutes, the apparatus was cooled, the boat removed, and the soluble matter in the residue extracted with water. After removing the insoluble portion by filtration, the filter was burned off and the resulting mass was returned to the apparatus for further treatment. While this was going on, the filtrate was tested, and vanadic acid found in it.

The treatment of the residue replaced lasted thirty minutes and effected the removal of more vanadic acid. On repetition of the extracting and testing, vanadium was again found in the soluble portion, and yet a third treatment failed to effect a separation.

Exp. 11. This experiment was carried out as was No. 10, using a different sample of material prepared in the same way. Two treatments on the insoluble residue failed to eliminate all of the vanadium.

Exp. 12. The general plan followed was as before in Exps. 10 and 11, but no heat was applied. It was found that several hours of treatment, during which the soluble matter was twice removed, resulted in an incomplete separation.

Exp. 13. Returning to the earlier method, the first part of the action of the acid gas was in the cold, then this was followed by gentle heat, until the substance in the boat liquified. At this point it was removed and extracted as before outlined. The solution gave a reaction for vanadic acid, and the residue yielded more on subjecting it to another treatment with hydrochloric acid gas. The extract

from this, however, showed no coloration on the addition of hydrogen peroxide. But the separation was not satisfactory because of the vanadic acid remaining in the water extract.

Exps. 14 *and* 15. In the hope that the presence of some other acid would in some way help to a better separation, the material used in these experiments contained phosphoric acid, co-precipitated as was the vanadic acid. But no greater success attended these efforts, after extended treatments as outlined in the other experiments, and with similar variations.

This uniform series of failures seems to justify the verdict that a separation is not possible by the methods followed, and so the study of iron compounds was abandoned.

The interfering causes seem to be: (1) The partial volatility of ferric chloride at temperatures not greatly exceeding 100°. (2) A formation of protecting layers of ferric or ferrous salts, thus preventing contact with the stream of acid gas. (3) The partial reduction of vanadic acid to a lower oxide which is not sensitive to the action of the reagent used. (4) The frequent repetitions necessary make the plan tedious, cause loss of material and give no great aid.

Vanadic Acid from Aluminium.

The material used for the prosecution of these experiments was most conveniently prepared as was that for iron. An excess of the aluminium was precipitated from a hot solution by ammonia, in presence of vanadic acid. The excess of hydroxide was necessary to take up all the vanadic acid. The gelatinous mass was washed, dried and ignited. The granular material was thoroughly powdered in a mortar, and re-ignited.

The vanadate so obtained was used for the following tests, without attempting to determine how the vanadic acid was present, though it was most likely as a "meta"-salt, these being generally obtained by precipitation.

Hydrogen peroxide was not used as a reagent for vanadic acid until Exp. 6.

Exp. 1. About 0.3 of a gram of material was placed in a porcelain boat, and this placed in the same apparatus used in the experiments on iron. The stream of hydrochloric acid gas was allowed to act in the cold for fifteen minutes. The contents of the boat, previously of a creamy white color, assumed a dark red hue, and water of reaction began to condense in the anterior end of the tube, and with it vanadic acid. The application of heat caused a more rapid action, with a whitening of the boat's contents. At the end of twenty minutes the reaction had greatly diminished, therefore the heat was raised considerably during the next hour. The total time of the action was one hour and thirty-five minutes.

When the apparatus was cool, the contents of the receiver were evaporated, and there remained crusts of vanadic acid. In order to test the residue in the boat, which should have been aluminium chloride only, in the event of a complete reaction, the contents were fused with a mixture of sodium carbonate and sulphur, the fusion taken up in water, and the aluminium precipitated out as basic carbonate by a stream of carbon dioxide. Any vanadium present should be as a sulpho-salt in the filtrate, therefore this was poured into dilute sulphuric acid and digested on a water bath for some time, when a brown precipitate of vanadium sulphide was obtained. Hence the separation was not complete.

Exp. 2. The conditions were about the same as in Exp. 1, save that the time was greatly lengthened, being three hours. During the action of the acid gas, there was an

evolution of chlorine indicating a reduction, probably in the vanadate, as aluminium compounds cannot be reduced to a lower valency. When the test used in Exp. 1 was applied to the residue, some vanadium sulphide resulted

The temperature used did not seem to be high enough to sublime aluminium chloride.

Exp. 3. So soon as the substance was placed in the apparatus a gentle heat was applied, and this caused a rapid reaction with the hydrochloric acid, both water and vanadic acid condensing in the anterior portion of the tube. At the end of an hour the experiment was discontinued, and the residue tested, with the result that vanadium was found.

Exp. 4. The failure to remove all of the vanadium by the simple treatment adopted, caused a modification of the method formerly used, in that after a half an hour, during which gently increasing heat was applied, the apparatus was cooled, the boat removed and its contents evaporated to dryness with nitric acid. It was then replaced and treated with the acid gas for twenty minutes. This evaporation process was twice repeated, each time followed by half an hour of action by hydrochloric acid gas, at moderate heat.

At the end of the fourth treatment, the receiver contents left no solid matter on evaporation, but the residue gave vanadium sulphide by the usual test used above.

Exps. 6, 7 *and* 8. These experiments require no detailed notice, save that, by use of the hydrogen peroxide test, an apparant separation was effected, as far as the soluble portion of the residue showed. The colorless solutions of aluminium salts make this test especially easy of application.

These favorable results seemed to justify the prosecution of quantitative analyses, and exps. 9-13, inclusive, were such attempts. The analyses were so unsatisfactory, however, that they were finally abandoned to take up a more

thorough study as to the qualitative separation.

With the foregoing experiments on aluminium, as with the earlier ones on iron, the composition of the insoluble part of the residue was not sufficiently determined, and just there the trouble lay. Theoretically, were the action complete, both as to the expulsion of vanadic acid and conversion of all oxide into chloride, there should have been no insoluble residue. As this condition was not attained, it seemed advisable to investigate that insoluble portion thoroughly, by getting it into solution by fusing with sodium carbonate. Such a solution after acidifying with sulphuric acid could be easily tested with hydrogen peroxided. It was found by special tests that the sodium carbonate did not contain vanadic acid, and that aluminium salts and carbon dioxide were not deleterious to the reaction of vanadium with hydrogen peroxide.

Exp. 14. A small portion of the usual material was subjected to the action of hydrochloric acid gas for a period of forty minutes, at a very gentle heat. The usual evolution of water vapor, vanadic acid and chlorine took place, and the heat was finally high enough to cause the separation of a faint white sublimate (of ammonium salts?) just over the boat.

On cooling and removing the residue, part of it was subjected to the fusion and testing as outlined above. Strong evidence of vanadic acid was found.

The remainder of the residue was evaporated to dryness with nitric acid, and subjected to the action of the hydrochloric acid for a half an hour at a moderate heat. At the end, although no vanadium was found in the receiver, traces were yet in the residue; thus indicating that the vanadium held after the first treatment was no longer acted on.

Exp. 15. The first treatment to which the residue was subjected lasted one hour and ten minutes, the procedure being as in Exp. 14. A portion of the residue when tested

showed vanadic acid. A second treatment was applied for forty-five minutes to the remainder of the residue, after it had been evaporated to dryness with nitric acid. The contents of the boat were again tested as before, with hydrogen peroxide. Traces of vanadium were found.

Exp. 16. In order to test the effect of larger quantities of material, a small boat was used, and nearly filled with the compound. Before treatment it was vaporated to dryness with nitric acid. After an hour's treatment in the hydrochloric acid gas, with gradually increasing heat, the residue gave a very strong test for vanadium. Hence it would seem that increasing the quantity of material makes the separation even more difficult.

Exp. 17. About 0.2 gram was subjected to two treatments of a half hour's time each, the first being supplemented with a nitric acid evaporation. The temperature was quite high at the end. But it was found that the second treatment failed to remove any of the vanadium left after the first.

Exp. 18. The same procedure was used as in Exp. 17, but the residue after the second treatment was taken to dryness with nitric acid and again placed in the apparatus for an hour and forty minutes. However, only a partial separation resulted.

As is the case of iron, there seems to be no satisfactory separation attainable by this method. The cause of the failure is not apparent, but it may be in some way related to the reduction accompanying the evolution of chlorine noticed throughout. This phenomenon was observed with iron, and with those metals subsequently studied.

Vanadic Acid from Manganese.

The material used in the first tests was prepared in the same way as the iron and aluminium compounds. The precipitate so obtained proved inconvenient to handle, and was therefore used in but two experiments. For the others, a meta-vanadate of manganese was prepared by adding ammonium vanadate to a hot solution of manganous sulphate. Though the precipitation was incomplete, enough was obtained for several analyses.

All precipitates were washed, dried, ignited, and excepting that used in the first experiment, thoroughly pulverized.

Exp. 1. The substance here used was that precipitated by ammonia. A portion was placed in the boat without previous grinding, it being in a fine granular condition. Even in the cold the hydrochloric acid acted on it, driving off vanadium, water and chlorine, while the residue began to turn black.

At the end of fifty minutes, the boat was removed and a portion of its contents treated with water. The resulting solution being too strongly colored by manganese chloride to test directly, a second portion of the residue was fused with sodium carbonate, taken up in water, and acidified with dilute sulphuric acid. On standing for some time the color was sufficiently weak to allow of testing with hydrogen peroxide, which proved the presence of vanadium.

Exp. 2. The same compound was used as in the previous test, but it was thoroughly ground. This time a gentle heat was applied, which augmented the intensity of the reaction. On testing the residue at the expiration of a half hour, vanadium was found, but no manganese had passed into the receiver.

Exp. 3. This experiment was conducted with the "meta" salt prepared as stated above. 0.121 gram was placed in

a boat, dried in an air bath at 90°–110° for an hour, and then placed in the apparatus for treatment with the hydrochloric acid gas. As before, the reaction began in the cold but was hastened by applying heat. Chlorine was evolved and the natural brown color of the substance changed to a green. A few moments later, there began to form a sublimate of faint yellowish green needles just beyond the boat. The crystals had a strong lustre and were ramified.

At the end of an hour and a half the substance in the boat had whitened somewhat, and no further reaction seemed going on. The residue was completely soluble, and therefore an attempt was made to analyse it quantitatively, but the results were far low, and much difficulty was experienced in weighing the vanadic acid obtained from the receiver, owing to the ease with which it was reduced while evaporating. The experiment was abandoned.

Exp. 4. The material used was prepared by adding the manganic solution to the solution of vanadic acid, thus reversing the first order. When dried and powdered, the substance had a light yellow color, which darkened on strong ignition. The substance did not alter in weight on standing in the air.

0.244 gr. was placed in the apparatus, and gradually warmed before admitting the hydrochloric acid gas. The reaction began after some little time and proceeded slowly. The acid and the heat were discontinued after forty minutes, and the boat was allowed to stand in the apparatus for nearly twenty hours. When the experiment was resumed, more vanadium came off, under gentle heating, and a good flow of gas. The heat was raised gradually during the next half an hour until it became quite intense.

The boat contents were brown when cold, and were partially soluble in water. On adding a little hydrochloric acid, all dissolved, and in this solution hydrogen peroxide gave a very strong affirmative test for vanadium.

Exp. 5. 0.3 gram of the same material was used, and treated as in Exp. 4 for a period of one hour. The residue was but little soluble in water, but disappeared on acidulating with sulphuric acid. Both the peroxide and the zinc reduction test proved the presence of vanadium.

This closed the experiments with manganese derivities, and the only point to be emphasized in this connection, after calling attention to the failure, is that the sublimate noticed in preparing vanadic acid from endlichite residues, was again obtained, though it attracted no particular attention at the time.

Vanadic Acid from Zinc.

For the experiments with zinc vanadate, a salt was prepared by precipitating the zinc from a solution of its acetate with sodium meta-vanadate, washing, drying, igniting and grinding, as before. The powder had a yellowish color.

Exp. 1. A portion of the substance was treated in the hydro-chloric acid gas in the cold for ten minutes, and then a gentle heat was applied. The reaction was vigorous. Some moisture seemed to remain in the boat, being held by the zinc chloride perhaps. After the reaction had proceeded forty minutes, the residue was white in spots only, the greater part being colored green, indicating a retention of vanadium as a lower oxide.

The experiment was discontinued after an hour and ten minutes, and when the residue was tested, it showed vanadium.

Exp. 2. The apparatus was first thoroughly dried, the substance introduced, and warmed at a gentle heat, and then the flow of gas begun. However, after treatment for an hour and twenty minutes, all the vanadium was not volatilized.

Exp. 3. The same method was adopted here as in Exp. 2, except that the heat was more intense, causing the contents of the boat to liquify. The treatment lasted two hours, and the boat contents on cooling appeared as a glassy mass, in which there were spots of green. The latter failed to dissolve in water, but went up in acid, in which solution vanadium was found by the use of peroxide of hydrogen.

Exp. 4. With this experiment, the use of a thermometer was begun, and it proved a useful factor thereafter in the fixing of conditions. It was placed in the apparatus through a hole in the stopper bearing the inlet-tube for the acid gas. By allowing the bulb to project over the boat, the temperature of the reaction was observed.

About 0.1 gram was weighed into the boat, and after forty minutes of treatment, during which time the heat became quite high, the substance finally appeared as a green crust. Chlorine was disengaged during the reaction. When the boat had cooled, it was removed, treated with nitric acid, evaporated to dryness, and replaced for further action. At a temperature of 45° a violent spattering took place, followed by melting. At 120° it again hardened, and at 180° a gray-green crust remained which refused to yield up all its vanadium.

The negative results again obtained are probably due to some of the same causes already given: (1) Reduction of the vanadate; (2) the protecting layer formed by zinc chloride.

Vanadic Acid from Barium.

To bring barium and vanadic acid together for the three experiments recorded, ammonium vanadate was added to a solution of barium chloride. Cold solutions were found to give far more complete precipitations. The ignited salt was pale yellow after powdering.

Exp. 1. Hydrochloric acid gas acted vigorously enough in the cold to cause the thermometer to show a rise of several degrees. On the application of a low heat, vanadium was rapidly expelled from the salt, and its superficial layer became white. The experiment continued an hour, and the highest temperature recorded was 230°.

When the boat was removed and inspected, the underlying part of the residue was found to be green in color, and this portion was only partly soluble in water. When strong hydrochloric acid was added to the water, this insoluble residue slowly dissolved to a yellowish green solution, and the usual hydrogen peroxide test gave strong indications of vanadium.

Exp. 2. 0.214 gr. was treated as before, for forty minutes, the residue then tested and vanadium was found. The remaining portion was evaporated to dryness with nitric acid, and the treatment with the acid gas repeated for an hour, with a maximum temperature of 170°. The orange colored residue showed traces of vanadic acid.

Exp. 3. The substance, which weighed 0.125 gram, was first evaporated to dryness with nitric acid, and then heated in an air bath to 100° for some time. It was transferred to the apparatus and there acted on by the hydrochloric acid gas for one hour and twenty minutes; the temperature finally registered was 190°. The nitric acid evaporation was then repeated, followed by thirty minutes more under hydrochloric acid gas. But the separation could not thus be completed.

This fourth series of experiments confirms the others in showing that the last traces of the vanadium are in some way tenaciously held by the metal, or that it is reduced to some involatile oxide.

Vanadic Acid from Lead.

The ill success attending upon the attempts to separate this acid from iron, aluminium, manganese, zinc and barium, made it desirable to turn to the derivitives of this metal, lead, it being of especial interest because it is the chief base associated with vanadium in the mineral kingdom. This interest was augmented by the success Pullman had in separating vanadic acid from the mineral endlichite and it was hoped that here at least, the monotonous negative results would be relieved. Though the desire was not fully materialized as to separations, the phenomena which appeared make this division the most important and also the most puzzling in the whole series.

Considerable variation will be found as to the material used because of the more extended study made. The substances analyzed were:

(a) Lead vanadate, precipitated from a solution of lead acetate by ammonium vanadate.

(b) A substance of indefinite composition made by fusing together vanadic acid and lead peroxide.

(c) A portion of (b) fused with lead chloride.

(d) The mineral endlichite; reported usually as an arsenovanadate of lead, in which the ratio of As : V=I:I. It also contains chlorine, phosphorus and metals in traces.

(e) Vanadinite, a mineral, of the same general composition as endlichite, but without more than small quantities of arsenic; or even none may be present.

Exp. 1. The substance (a) was used, and it was in the form of a light brown powder. The time of treatment was forty-five minutes and the highest temperature was 160°. At 75°-80°. there was a formation of the crystalline sublimate previously observed with manganese, and elsewhere, and chlorine was also generated by the reaction. Hydrogen peroxide applied to a solution of a portion of the residue gave a marked test for vanadium.

Exp. 2. In this experiment the material (b) was used, after previous evaporation to dryness with nitric acid, and heating to 110°. Reaction began with the acid gas at about 65°, with an evolution of water, vanadic acid and chlorine, and a subsequent formation of the sublimate as in Exp. 1.

At higher temperatures, the residue began to turn from grayish to nearly white. Time, forty-five minutes; maximum temperature, 190°. The test for vanadium in the residue was doubtfully negative.

Exp. 3. Another portion of (b) was subjected to thirty minutes treatment in the hydrochloric acid gas. The maximum temperature attained this time was 80°, and at this point the apparatus was cooled and the residue tested. Another treatment was found necessary, and so the boat was replaced for an hour, during which time the heat rose to 220°. But a complete separation did not result.

Exp. 4. This experiment gave a partial expulsion after several treatments amounting to two and one-half hours.

In experiments 2, 3 and 4 also, the sublimate was obtained at about 70°-90°.

Since no separation seemed possible with the simple lead vanadate, it was determined to try the effect of some of the other constituents of endlichite if present in these synthesized salts. This lead to the preparation of material (c), as given, hence it consisted of lead vanadate and lead chloride.

Exp. 5. The fused mass (c) was ground fine, and then evaporated to dryness with nitric acid. After forty-five minutes action of the hydrochloric acid gas no satisfactory separation came about. Again the sublimate appeared.

In the light of these continued negative results, it now seemed advisable to review carefully the work done on endlichite, from which Pullman had reported a separation, and if possible, determine the causes for his success, if suc-

cess it were, and apply these conditions to other cases.

Without repeating the supposed composition of endlichite, it may be said that the inefficiency of the lead chloride, as demonstrated by Exp. 5, led to speculation regarding the function of the arsenic, present in amount equivalent to the vanadium. It was thought that this being likewise volatile, would aid in the passage of the vanadium.

In order to check the work on endlichite three experiments were tried on samples of that mineral, varying the conditions of temperature, and with and without previous evaporation with nitric acid. Without going into details, it may be said that the work confirmed Pullman's quite uniformly, and a separation can be had in a half hour's time, if less than 0.4 gr. of mineral be finely ground and evaporated with nitric acid. Greater quantities make the separation less certain. The maximum temperature reached (200°) is great enough to cause some of the iron to pass over into the receiver.

It may not be out of place here, though perhaps not pertinent, to report an experiment conducted after thoroughly moistening the substance with water. In this case, the whole of the vanadium could not be removed, even at a high temperature and with long treatment. The residue remained green, and the crystalline sublimate did not form until about 130° had been reached. A violent reaction and evolution of chlorine took place at 40°.

The question again asserts itself: What causes the vanadium to deport itself so differently in its lead derivitives? Should the answer be found in the presence of arsenic as suggested above, its truth could be demonstrated by synthesizing an arseno-vanadate and making a test, or in a way, it could be shown by negative evidence if one could find a natural lead vanadate, free from arsenic, which would not give up its vanadic acid.

The latter course was adopted in part by purchasing some crystals of the mineral vanadinite, which it was hoped, would arsenic-free. But, although arsenic was found in it by Marsh's test, it behaved entirely differently from the endlichite, in that it seemed to retain traces of vanadium with a stronger hold than any substance yet tested. In no case was a complete separation obtained, though many changes of procedure were tried. These in detail are the same as have been often repeated, and will be omitted therefore. In two experiments, however, four and five treatments were undergone by the same sample, using the evaporation with nitric acid also.

Besides its persistent holding back of vanadium, the mineral vanadinite exhibited another difference from endlichite; no crystalline sublimate came out of it. This seemed strange at once, because the two minerals were thought to be the same qualitatively, at least. This fact centers the interest on a closer comparison of these substances, especially since they are typical of opposite results, and that point will be discussed in the second section of this paper.

Vanadic Acid from Nickel and Cobalt.

The solution of vanadic acid used heretofore was now exhausted, and that on hand was in solid form, and not so pure. It had been used in preparing (b) under lead.

No satisfactory precipitates could be obtained by solutions of this vanadic acid with nickel and cobalt salts, and therefore it was merely fused with an excess of their oxides or nitrates, and the resulting masses broken up thoroughly and ignited again.

Experiments. The experiments performed were quite similar to those frequently recorded, as to methods used. There were no satisfactory separations obtained.

To test the colored solutions the cobalt and nickel were

previously precipitated by hydrogen sulphide in presence of acetic acid.

Both cobalt and nickel gave small quantities of the sublimate noted with manganese and lead.

The first section of this paper closes with the report on nickel and cobalt, the continued negative results making it useless to continue with simple salts until some condition could be located which would open the way to success. Though, to make the work more complete, Smith and Hibbs' work on the alkali vanadates should be extended to other members of Group I.

No light can be thrown on the form in which vanadium is retained in these compounds, but the evolution of chlorine indicates a reduction, and it is likely that an oxide as low as the tetroxide remains, or one intermediate between that and the pentoxide.

The residues were generally green, or gave green solutions in acids. This reduction may therefore be related to that described by Gibbs as taking place in hydrochloric acid solutions.

SECTION II.

The Occurrence of Molybdenum in the Mineral Endlichte.

Throughout the first section of this thesis there was frequently noted the appearance of a certain needle-like sublimate on passing hydrochloric acid gas over various compounds of vanadium and metals, such as manganese, lead, cobalt and nickel, and from the residues first worked for vanadic acid. But by far the greatest yield was from the mineral endlichite.

That this behavior constitutes a marked distinction from vanadinite was also recorded in the other section, where the minerals were contrasted as to their deportment with hydrochloric acid gas, the latter stubbornly holding the last traces of vanadium.

Hence it was decided to investigate this compound (*i. e.*, sublimate) in order to discover its nature and bearing on the difference exhibited by the minerals. Naturally it was assumed at first that this sublimate was in the nature of an oxychloride of vanadium, and to determine its composition and the conditions necessary to its formation might mean an establishing of the procedure to be followed in obtaining separations from other compounds. That it was purely a vanadium compound was not doubted.

While the nature of the compound is established herein, no evidence can be given that it actually functions in the separation of the vanadic acid, though it is a reasonable speculation.

In the previous handling of this sublimate, no especial note was made of its properties, hence it was necessary first of all to isolate it in sufficient quantity for analysis. It has been described as very pale yellowish green needle-like crystals, considerably branched. They formed first at temperatures between 70°-100°, and slowly increased during the experiments, and direct heat in a stream of the acid gas caused them to sublime to a compact woolly mass. Standing in the air caused them to disintegrate to a green amorphous delequescent substance.

The isolation of such a compound as roughly described above, must at once involve difficulties, and these are enhanced by the fact that while this sublimate is forming, other more volatile products are leaving the mineral, and these must be prevented from contaminating the crystals. Then the proper conditions of temperature and gas flow must be found. Experiments showed that too little heat caused the

condensation of vanadic acid, which could not again be driven off, while too much heat caused a decomposition of the crystals. Again, a strong current of acid gas prevented control of their condensation; a slow current allowed overheating.

To cover these weak points took much experimenting which resulted in many failures. The most satisfactory apparatus I was able to design and operate gave about eight perfect samples out of thirty or more. The others were partly decomposed, or contaminated with vanadic acid.

The apparatus finally adopted was a soft glass tube, near the anterior end of which is a chamber, or bulb, about four inches in length was made by constricting the tube at two points this distance apart. The anterior opening of the tube was connected by a bent glass tube of small size, to a beaker of water which served as a receiver. The posterior end of the tube was, after introducing the mineral in a boat, joined as usual to the hydrochloric acid gas generator. Heat was applied just under the boat, while the tube was warmed gently the whole of its length, so that none of the more volatile products would condense. When all of the sublimate was formed just behind the bulb, the boat was rapidly removed, the cork replaced and the current of gas started again. By means of a Bunsen burner held in the hand, the sublimate was carefully driven into the bulb. This was rapidly sealed, using precautions to prevent the receiver liquors drawing up into the tube.

During the prosecution of this work, which was extremely slow because of failures and small yields, together with the necessity of arranging a new tube after each trial, it was suggested that this sublimate bore a marked resemblance to Debray's oxychloride of molybdenum, obtained by the same procedure from its trioxide. The general aspect of the two was quite identical, and its appearance, noted throughout the previous section, would be accounted for by contamina-

tion from the endlichite residues, and occasional co-precipitation of a vanadate and molybdate.

This possibility became so interesting that the following experiments were at once undertaken with a view toward a solution of the question:

The contents of a bulb on standing in the air, rapidly changed as already described, to a green delequescent mass.

To test the solubility, the contents of another bulb were dropped into water. A colorless solution readily obtained; had the compound contained vanadic acid, there would have been an orange coloration. A lower vanadium oxide would have been green. On adding hydrogen peroxide to this aqueous solution, there was an immediate change of color to yellow, which is the test for molybdenum, and not vanadium, the color test of which is red.

When a few crystals were added to concentrated sulphuric acid, the resulting solution was colorless, contra-indicating vanadium again. This acid solution was heated on the lid of a platinum crucible until fumes came off, and then cooled. On the addition of a little alcohol, a beautiful deep blue color resulted. This is said to be characteristic of molybdenum, in distinction from vanadium, titanium and tungsten. (Fresenius, loc. cit.)

The action of ammonia on the sublimate again indicated the absence of vanadium. The first drop or two decomposed the compound and liberated a white powder, which dissolved in an excess of ammonia to a colorless solution.

Concentrated nitric acid also dissolved the substance readily, and on warming this solution, chlorine was evolved, (indicating an oxychloride) and a white crust collected. Debray's compound would be expected to conduct itself in this way.

When the nitric acid had been evaporated off, the white powder was gently ignited in a covered crucible for a few moments. There sublimed to the cooler part a beautiful

iridescent woolly mass, plainly molybdenum trioxide, and no vanadic acid was found.

The more characteristic tests above recorded were confirmed by repetition, and therefore it seems justifiable to assert that molybdenum is a constituent of the endlichite used, and that any vanadic acid prepared from it may contain molybdic acid, and hence give the sublimate from various synthesized vanadates.

Turning to the sample of vanadinite at hand, several tests showed no molybdenum, and this is confirmed by the lack of a sublimate in the analytical work done with hydrochloric acid gas.

This establishes one strong difference in composition between the two minerals, but does not connect that difference with their respective behaviors as to the separation of vanadic acid.

As was said in the introduction to Section I, the failure to report this element by those who handled it before was partly due to the lack of a direct test, and partly to the very similar behavior of vanadium and molybdenum in the processes to which the mineral was subjected.

Though this discovery is of no great importance, it is at least of interest to the mineralogist to learn if endlichite contains molybdenum normally, or if it be a mechanical admixture of some molybdate such as wulfenite, which occurs in the same localities. This point cannot be settled with specimens at hand, since they are all finely ground.

The presence of molybdenum in endlichite may or may not account for the complete elimination of vanadic acid from it by hydrochloric acid gas. The effect could be tested on synthetic compounds of vanadates with molybdates, with arsenates, and with both molybdates and arsenates.

And, finally, vanadium minerals should be generally tested for molybdenum, and molybdenum minerals might be investigated for vanadium, with the view of firmly establishing their natural relationships.